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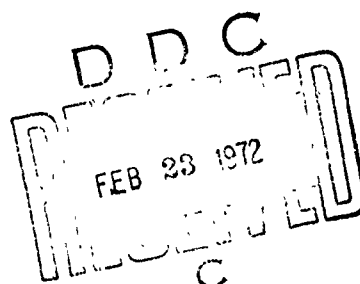
TECHNICAL REPORT No. 20

Polyurethane Elastomers Based on Hydroxyl-terminated Polybutadienes

**B E Brokenbrow
D Sims
J Wright**

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SUMMARY

Polyurethane elastomers prepared from hydroxyl-terminated polybutadiene polymers and copolymers have been assessed and compared with polyester and polyether urethanes. The effects of various diols and diamines as chain extenders and crosslinking agents and additions of carbon black to the hydroxyl-terminated polybutadienes have also been studied.

Hydroxyl-terminated polybutadiene urethane elastomers showed superior hydrolytic stability to the polyester and polyether urethanes selected for comparison; on the other hand, their resistance to petroleum (STP) was less satisfactory.

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1 INTRODUCTION

Polyurethane elastomers are usually prepared by reacting di- or polyfunctional hydroxyl-terminated polyesters or polyethers with di- or polyfunctional isocyanates. In general, polyurethane elastomers have good mechanical and electrical properties and show good resistance to oxygen, ozone and dry air at temperatures up to 75°C.

The properties of polyurethane elastomers may vary quite widely depending on their molecular weight, degree of crosslinking, intermolecular forces, stiffness of chain units, ease of rotation of chain segments and crystallinity. Polyurethane elastomers, however, suffer from certain inherent limitations. Polyester urethanes, for example, are sensitive to hydrolysis and solvent attack, while polyether urethanes are also susceptible to photo-oxidative degradation.

A possible way of overcoming some of these disadvantages might be to replace the polyester or polyether component with a medium molecular weight di- or polyhydroxyl-bearing hydrocarbon polymer such as polyisoprene or polybutadiene.

Although hydroxyl-terminated hydrocarbon homopolymers have been reported in the literature,^{1,2,3,4,5} hydroxyl-terminated butadiene homopolymers and copolymers with styrene and acrylonitrile, having molecular weights of over 2000, have only been available commercially in the United States since 1965.⁶ According to French⁷ four commercial organisations in the United States supplied hydroxyl-terminated polybutadienes during 1968. Two of these organisations used an ionic polymerisation method of preparation and two a free radical method.

The object of the present investigation was to assess four hydroxyl-terminated butadiene homopolymers and copolymers, supplied by Sinclair Petrochemicals Inc US, as components of polyurethane elastomers and to study their ageing characteristics after immersion in water and petrol (STF).

2 MATERIALS

The materials evaluated, of average molecular weight 2500 - 3500 with a hydroxyl functionality of 2.1 to 2.6, were as follows.

R.15M and R.45M	hydroxyl-terminated polybutadiene homopolymers
CS.15	a hydroxyl-terminated polybutadiene/styrene copolymer
CN.15	a hydroxyl-terminated polybutadiene/acrylonitrile copolymer

The properties of the materials supplied are listed in Table 1 below.

TABLE 1

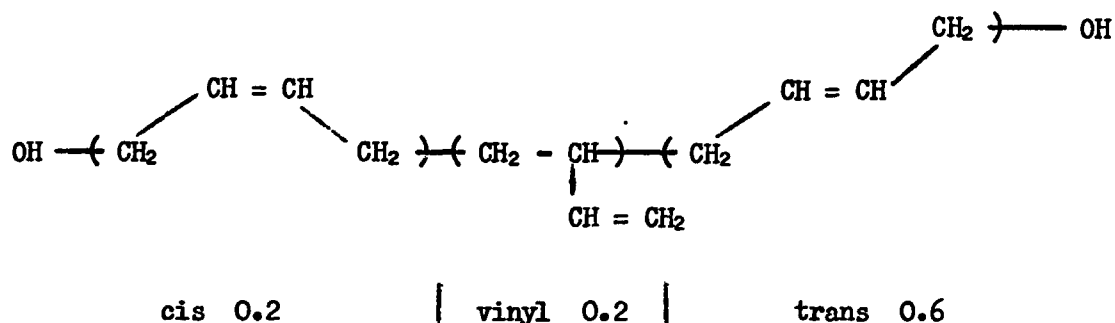
	R.15M Butadiene Homopolymer	R.45 M Butadiene Homopolymer	CS.15 Styrene Copolymer	CN.15 Acrylonitrile Copolymer
*Hydroxyl No (KOH mg/g)	38	43	36.5	32
**Hydroxyl Value (meq/g)	0.68	0.75	0.65	0.57
**Equivalent Weight	1470	1330	1540	1780
Viscosity, poise (30°C)	225	55	205	490
Non-volatile (4 h - 100°C)	99.9	99.9	99.5	99.5
Colour Visual	pale lemon	pale lemon	opaque white	orange

*Determined

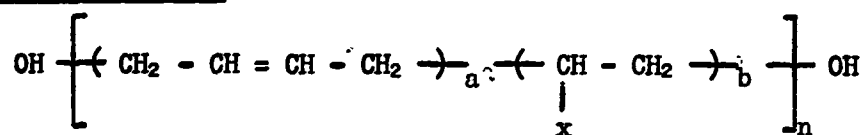
$$\begin{aligned} \text{**Calculated Hydroxyl value, millilitres} &= \frac{\text{Hydroxyl No}}{56.1} \\ \text{Equivalent weight} &= \frac{1000}{\text{Hydroxyl Value}} \end{aligned}$$

The structures of the materials are as follows.

R.15 M and R.45 M homopolymers



CS.15 and CN.15 copolymers



where x is phenyl for CS.15 butadiene/styrene copolymer

$$\begin{aligned}
 a &= 0.85 \\
 b &= 0.25 \\
 n &= 40 - 50
 \end{aligned}$$

or

where x is CN for CN.15 butadiene/acrylonitrile copolymer

$$\begin{aligned}
 a &= 0.85 \\
 b &= 0.15 \\
 n &= 55 - 65
 \end{aligned}$$

The polybutadiene microstructure of all the polymers is

trans - 1,4 60%, cis - 1,4 20%, vinyl 1,2 20%

3 GENERAL METHODS OF ELASTOMER PREPARATION

All the elastomers were prepared using toluene di-isocyanate (TDI)-Hylene T.I. supplied by Du Pont UK - a mixture of 80 per cent 2,4 and 20 per cent 2,6 isomers. Details of the elastomers are summarised in Table 2, detailed formulations and methods of preparation are given in Appendix B.

TABLE 2A

Hydroxyl-terminated Polybutadiene Elastomers P.1 - P.16

Elastomer Number	Prepolymer		Elastomer		
	Hydroxyl-terminated Polybutadiene	Ratio NCO : OH	Diol NCO : OH 1.1 : 1.0	Diamine NCO : NH 0.7 : 1.0	Carbon Black (a) (parts per hundred prepolymer)
P.1	R.45	1.0 : 1.0	-	-	-
P.2	R.15	1.0 : 1.0	-	-	-
P.3	R.15	1.09 : 1.0	2-ethyl hexane-1,3-diol**	-	-
P.4	R.45	1.08 : 1.0	"	-	-
P.5*	R.45	1.08 : 1.0	"	-	-
P.6	R.15	1.09 : 1.0	"	-	-
P.7	CS.15	1.09 : 1.0	"	-	-
P.8	CN.15	1.09 : 1.0	"	-	-
P.9	R.45	1.08 : 1.0	1,4-butane diol	-	-
P.10	R.45	1.08 : 1.0	1,5-pentane diol	-	-
P.11	R.45	1.08 : 1.0	1,2-propane diol	-	-
P.12	R.45	1.08 : 1.0	2-ethyl hexane-1,3-diol	-	-
P.13	CS.15	1.09 : 1.0	-	Flexzone 4L (b)	-
P.14	CN.15	1.09 : 1.0	-	"	-
P.15	R.15	1.09 : 1.0	2-ethyl hexane-1,3-diol	-	16
P.16	CN.15	1.09 : 1.0	"	-	16

(a) Vulcan 3F carbon black

(b) N,N'-bis-(4-dimethylpentyl)-p-phenylenediamine

* Elastomer prepared using dibutyl tin dilaurate

** P.3. Diol NCO : OH 1.3 : 1.0; P.4, 1.0 : 1.0

TABLE 2B

Polyether and Polyester Elastomers P.17 - P.24

Elastomer Number	Polyester	Moles	Polyether	Moles	Diol, Diamine or, Triol	Moles	TDI Moles
P.17	Diethylene adipate (mol wt 2000)	1.0	-	-	1,2,6-hexane triol	0.66	2.2
P.18	-	-	Propylene glycol (mol wt 2000)	1.0	1,2,6-hexane triol	0.67	2.33
P.19	Diethylene adipate (mol wt 2000)	1.0	-	-	butadiene epichlorhydrin	0.40	2.1
P.20	Diethylene adipate (mol wt 2000)	1.0	-	-	styrene epichlorhydrin	0.50	2.2
P.21	-	-	Tetramethylene glycol (mol wt 1970)	1.0	1,2,6-hexane triol	0.66	2.2
P.22	-	-	Tetramethylene glycol (mol wt 1970)	1.0	IIOCA*	*8.8 pph	2.06
P.23	Diethylene adipate (mol wt 2200)	1.0	-	-	1,2,6-hexane triol	0.66	2.1
P.24	Tetramethylene adipate (mol wt 2250)	1.0	-	-	1,2,6-hexane triol	0.66	2.1

*4,4'-methylene-bis-(2-chloroaniline) 8.8 parts per hundred of prepolymer

3.1 Elastomers P.1 - P.16 Based on Hydroxyl-terminated Polybutadiene Homopolymers and Copolymers

3.1.1 Elastomers P.1 and P.2

These were prepared by direct reaction between the hydroxyl-terminated polybutadiene polymers and TDI to give an NCO : OH ratio of 1.0 : 1.0.

3.1.2 Elastomers P.3 - P.16

These elastomers were prepared by a prepolymer method. The hydroxyl-terminated polybutadiene polymer, 1 mole, was reacted with TDI, 2.1 - 2.6 moles, to produce an isocyanate-terminated prepolymer with a free NCO content of 6 - 9 per cent. The prepolymers, with or without the addition of carbon black, were subsequently reacted with diols or diamines to give an NCO : OH ratio of 1.1 : 1.0 or NCO : NH ratio of 0.7 : 1.0.

3.2 Elastomers P.17 - P.24 Based on Polyethers and Polyesters

Polyesters (average molecular weight 2000, acid number < 1.0, hydroxyl number 55 - 65), were prepared in the laboratory by the reaction between diethylene or tetramethylene glycol and adipic acid.

Polyethers based on polypropylene and polytetramethylene glycols (average molecular weight 2000, acid number < 1.0, hydroxyl number 55 - 65), were obtained from commercial sources.

Most of the elastomers were prepared by a direct method in which 1 mole of polyester or polyether and 0.66 mole 1,2,6-hexane triol crosslinking agent was reacted with 2.1 to 2.2 moles of TDI. A few elastomers were prepared using polyether or polyester/TDI prepolymers and chain extended or crosslinked with experimental hydroxyl-bearing low molecular weight butadiene-epichlorhydrin or styrene-epichlorhydrin polymers, or alternatively 4,4'-methylene-bis-(2-chloroaniline).

3.3 Preparation of Elastomer Sheet

The reaction products were poured into PTFE coated steel trays and cured in an oven for 60 h at 70 - 90°C to produce sheets 220 x 150 mm, 2.5 mm thick. The casting properties and general appearances of the hydroxyl-terminated polybutadiene elastomers are summarised in Table 3.

TABLE 3

Elastomer Number	General appearance of elastomer
P.1	Good - pale yellow - no bubbles
P.2	" " " " "
P.3	" " " " "
P.4	" " " " "
P.5	Slightly overcured - ridges
P.6	Fair-good - pale orange - a few bubbles
P.7	Good - pale yellow - a few bubbles
P.8	" " " " "
P.9	Slightly incompatible - opaque white - no bubbles
P.10	Good - yellow - slow curing
P.11	Slightly incompatible - opaque white - no bubbles
P.12	Good - yellow - no bubbles
P.13	Fair - brown-black - isolated bubbles
P.14	" " " " "
P.15	Fair - black - some ridges - isolated bubbles
P.16	Fair - black - some ridges and bubbles

4 EXPERIMENTAL

British Standard type E dumb-bell test pieces (eight) were cut from the cast sheets and the width and thickness measured before exposure to the test conditions. Dumb-bells, in sets of four, were suspended in loosely stoppered glass tubes and exposed to some or all of the following environments for twenty-eight days.

Controls	Conditioned in air at 20°C
Hot/dry	Suspended in air at 80°C
Hot/wet	Immersed in boiled out distilled water at 80°C
*Standard Test Fluid	Immersed in Standard Test Fluid at 65°C according to BS 903 : Part A 16

The charged tubes were placed in circulating air ovens in which the temperature did not vary by more than $\pm 0.5^\circ\text{C}$ from the test temperature. After twenty-eight days' exposure the tubes and contents were removed from the oven and conditioned at room temperature for 24 hours before testing. After the conditioning period, the groups of four specimens were removed from the tubes, dried from a superficial liquid, and tested for hardness, moduli, extension at break and tensile-strength as quickly as possible. Hardness was measured using a micro-indentometer and the tensile properties on a Hounsfield Tensometer by British Standard Methods.^{9,10} Unaged control specimens cut from the materials were tested by the same methods, and the results used as "unaged" reference points.

5 RESULTS AND DISCUSSION

The mechanical properties of the elastomers before ageing for twenty-eight days are recorded in Table 4, Appendix A.

The percentage changes in the original mechanical properties of the elastomers after ageing are recorded in Table 5, Appendix A.

Many of the hydroxyl-terminated polybutadiene urethane elastomers possessed good hydrolytic stability, showing changes in hardness, moduli, tensile strength and extension at break, of less than 15 per cent after 28 days' immersion in water at 80°C. On the other hand, many of the polyester and polyether urethanes either disintegrated or showed considerable changes in original mechanical properties after immersion in water. Polyester urethanes P.19 and P.20 chain extended or crosslinked with experimental hydroxyl bearing butadiene-epichlorhydrin and methylstyrene-epichlorhydrin polymers were inferior to polyester urethanes prepared with conventional triols, for example, 1,2,6-hexane triol, especially after immersion in STF.

In general, the hydroxyl-terminated polybutadiene urethane elastomers were less satisfactory than the polyester and polyether urethanes in resisting STF at 65°C, as shown by the greater losses in tensile strength and extension at break of the

*Standard Test Fluid (STF) consists of a 70/30 v/v mixture of iso-octane and toluene and is intended to represent a standard "medium to high aromatics" content petrol.⁸

polybutadiene based elastomers.

5.1 Comparison of Polyurethanes based on Different Hydroxyl-Terminated Polybutadiene Polymers with Polyesters and Polyethers

Table 6 compares the initial mechanical properties and resistance to ageing of polyurethane elastomers prepared from four different hydroxyl-terminated polybutadiene polyurethane elastomers, all chain extended with 2-ethyl hexane-1,3-diol, with those of typical polyester and polyether urethanes.

Polyurethanes based on hydroxyl-terminated polybutadiene homopolymers, although having lower initial tensile strengths but similar hardness to the copolymers, showed the best all round resistance to water, judged by retention of their initial mechanical properties. Polyurethane elastomers prepared from hydroxyl-terminated polybutadiene homopolymers and copolymers were superior to polyester and polyether urethanes, although their resistance to STF was inferior.

5.2 Effect of Diols on the Properties of Hydroxyl-Terminated Polybutadienes Polyurethane Elastomers

Table 7 compares the initial mechanical properties and resistance to ageing of polyurethane elastomers prepared from a hydroxyl-terminated polybutadiene, chain extended with various diols.

Polyurethane elastomers based on a hydroxyl-terminated polybutadiene homopolymer, chain extended with a branched chain hydrocarbon 2-ethyl hexane-1,3-diol showed the best all round mechanical properties initially; elastomers based on 1,4-butane diol also showed good initial mechanical properties and were superior to elastomers based on 1,5-pentane and 1,2-propane diols. All the elastomers apart from those extended with 1,4-butane diol, judged by changes in their initial mechanical properties, showed satisfactory resistance to water. Elastomers based on 1,4-butane diol were not very satisfactory in water and also showed the greatest change after immersion in STF.

5.3 Comparison of Diol and Diamine Chain Extenders in Hydroxyl-terminated Polybutadiene Polyurethane Elastomers

Table 8 compares the initial mechanical properties and resistance to ageing of polyurethane elastomers based on hydroxyl-terminated butadiene/styrene and butadiene/acrylonitrile copolymers, chain extended with 2-ethyl hexane-1,3-diol and N,N'-bis-(dimethylpentyl)-p-phenylene diamine.

Elastomers based on hydroxyl-terminated polybutadiene copolymers, chain extended with diols, showed higher tensile strengths and extensions at break compared to those chain extended with diamines, although diamine extended elastomers were initially rather harder.

The water resistance of the diol extended elastomers, especially P.7 based on a butadiene/styrene copolymer, were superior to P.13 and P.14 chain extended with a diamine. In addition, the resistance of diol extended elastomers to STF was slightly better than those extended with diamines. The superior initial hardness of diamine extended elastomers, compared with those extended with diols,

may be attributable to the fact that as the hydroxyl-terminated polybutadiene resins have a functionality exceeding two, crosslinking with diols would occur via allophanate and urethane reactions, while with diamines crosslinking via allophanate, biuret and urea reactions can occur. However, their inferior tensile strengths compared to diol extended elastomers is somewhat surprising, although it is likely that their properties could be improved by using a higher NCO : NH ratio.

5.4 Effect of Carbon Black Additions to Hydroxyl-Terminated Polybutadienes Polyurethane Elastomers

Table 9 compares the initial mechanical properties and resistance to ageing of polyurethane elastomers based on hydroxyl-terminated butadiene/styrene and butadiene/acrylonitrile copolymers, with and without the addition of carbon black.

Although no attempt was made to determine the optimum quantity or type of carbon black necessary to reinforce the elastomers, the addition of 16 parts per hundred carbon black to P.16, a butadiene-acrylonitrile/TDI prepolymer, appeared to be beneficial, both from the point of view of increasing tensile strength (by about 50 per cent) with relatively small losses of extension at break (about 20 per cent). Similarly the retention of mechanical properties of the carbon black filled elastomer after immersion in water was superior to those of the unfilled elastomer. Although no reinforcement was observed with P.15, a butadiene/styrene copolymer containing carbon black, the retention of tensile properties of this material after immersion in water were rather better than those of the unfilled elastomer.

TABLE 6

Elastomer Number	Type	Initial Properties		% change in mechanical properties after 28 days in					
				Water at 80°C			STF at 65°C		
		Tensile Strength, 1 IN/IN ²	Ext at break, %	Hardness, BSO	Tensile Strength at break	Extension at break	Hardness	Tensile Strength at break	Hardness
P.5	PBD homopolymer	7.8	355	80	- 2.6	-14.8	- 5.5	-85.4	-52.6
P.6	PBD homopolymer	7.1	265	81	0.0	- 2.7	- 5.0	-84.8	-48.3
P.7	PBD styrene copolymer	10.7	205	80	-16.3	-14.1	- 3.7	-82.6	-50.2
P.8	PBD acrylonitrile co-polymer	11.5	320	73	-38.0	-18.6	-19.9	-87.6	-58.1
P.17	Polyester (polydiethylene adipate)	4.5	840	< 30	Disintegrated				
P.24	Polyester (polytetramethylene adipate)	17.4	335	90	Disintegrated				
P.18	Polyether (polypropylene glycol)	2.37	235	55	Disintegrated				
P.22	Polyether (polytetramethylene glycol)	18.9	810	71	-97.8	-95.2	-57.8	- 5.8	+13.1
									+ 2.8

TABLE 7

Elastomer Number	Type Diol	Initial Properties			% change in mechanical properties after 28 days in					
		Tensile Strength, IN/mm^2	Ext at break, %	Hardness, BSO	Water at 80°C			STP at 65°C		
					Tensile Strength at break	Extension at break	Hardness	Tensile Strength at break	Extension at break	Hardness
P.9	1,4-butane diol	7.2	255	57	-47.1	+118	-28.1	-95.3	-52.9	-53.2
P.10	1,5-pentane diol	1.86	45	81	+10.0	-11.1	+ 4.9	-71.6	-44.4	-16.1
P.11	1,2-propane diol	3.03	105	81	+ 2.27	-65.1	0.0	-72.8	-58.0	-25.9
P.12	2-ethyl hexane-1,3-diol	7.2	210	78	- 3.7	- 9.4	- 2.6	-77.7	-54.3	-30.7

TABLE 8

Elastomer Number	Polymer and Chain Extender	Initial Properties			% change in mechanical properties after 28 days in					
		Tensile Strength, MN/m ²	Ext at Break, %	Hardness, BSO	Water at 80°C			STF at 65°C		
					Tensile Strength	Extension at break	Hardness	Tensile Strength	Extension at break	Hardness
P.7	Butadiene/styrene diol	10.7	205	80	-16.3	-14.1	- 5.7	-82.6	-50.2	-55.0
P.8	Butadiene/acrylonitrile diol	11.5	320	73	-38.0	-18.6	- 5.5	-87.6	-58.1	-64.5
P.13	Butadiene/styrene diamine	7.4	170	96	-47.1	+118	-28.1	-95.3	-52.9	-53.2
P.14	Butadiene/acrylonitrile diamine	7.2	195	87	-70.0	+120	-45.0	-95.8	-50.7	-45.0

TABLE 9

Elastomer Number	Polymer and chain extender	Carbon Black	Initial Properties			% change in mechanical properties after 28 days in					
			Tensile Strength, MNV/mm ²	Extension at break, %	Hardness, BSO	Water at 80°C			STF at 65°C		
						Tensile Strength	Extension at break	Hardness	Tensile Strength	Extension at break	Hardness
P.7	Butadiene/styrene diol	Nil	10.7	205	80	-16.3	-14.1	- 5.0	-82.6	-50.2	-35.9
P.8	Butadiene/acrylonitrile diol	Nil	11.5	320	73	-38.0	-18.6	- 5.5	-87.6	-58.1	-31.5
P.15	Butadiene/styrene diol	16 pph	8.8	340	87	-11.8	- 8.8	-20.7	Too swollen to test		
P.16	Butadiene/acrylonitrile diol	16 pph	16.5	255	83	- 5.1	- 2.7	- 7.2	-79.8	-45.6	-34.9

6 CONCLUSIONS

Hydroxyl-terminated polybutadiene homopolymers and copolymers are useful additional polyfunctional hydroxyl bearing components now available for the preparation of polyurethane elastomers. These materials appear to be of particular value in the formulation of polyurethane elastomers for applications where resistance to hydrolysis is important. The hydrolytic stability of polyurethane elastomers prepared from hydroxyl-terminated polybutadiene polymers, judged by laboratory tests, was superior to that of the polyester and polyether urethanes selected for comparison; however the resistance of the polybutadiene urethanes to petrol (STP) was less satisfactory. In this respect, urethane elastomers offering a compromise between acceptable hydrolytic and fluid stability might be achieved by blends of polytetramethylene glycol ether and polybutadiene homopolymers. In addition, the present investigation indicated that the performance and physical properties of polyurethane elastomers based on hydroxyl-terminated polybutadiene polymers could be upgraded by additions of carbon black and further investigations in this direction are also proposed. The long term outdoor durability of elastomers based on hydroxyl-terminated polybutadienes is being studied and the results will be reported at a later date, in conjunction with investigations which are at present being made at these laboratories, to correlate the performances of polyurethane elastomers with their chemical structure.

According to Richards,¹ who has prepared hydroxyl-terminated polybutadienes on a small scale at this Establishment, there would be little difficulty in scaling up the preparation for semi- or full commercial production should the need arise.

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APPENDIX A

MECHANICAL PROPERTIES

TABLE 4

Mechanical Properties of Polyurethane Elastomers (Unaged)

Elastomer		Tensile Strength, MN/m ²	Extension at break, %	Modulus at 100 per cent extension MN/m ²	Hardness, BS ^o
Number	Type				
P.1	OH-PB	0.10	250	0.03	< 30
P.2	"	0.65	100	0.65	49
P.3	"	8.40	90	-	86
P.4	"	3.41	115	2.50	58
P.5	"	7.80	355	3.65	80
P.6	"	7.10	265	3.48	81
P.7	"	10.70	205	4.76	80
P.8	"	11.50	320	3.00	73
P.9	"	7.20	255	0.62	57
P.10	"	1.86	45	-	81
P.11	"	3.03	105	2.83	81
P.12	"	7.20	210	3.78	78
P.13	"	7.40	170	6.17	96
P.14	"	7.20	195	3.89	87
P.15	"	8.80	340	4.10	87
P.16	"	16.50	255	6.07	83
P.17	Polyester	4.50	840	0.03	< 30
P.18	Polyether	5.24	135	0.41	45
P.19	Polyester	2.37	235	0.76	55
P.20	"	1.41	255	0.34	44
P.21	Polyether	2.34	135	2.00	71
P.22	"	18.90	810	3.06	71
P.23	Polyester	1.72	350	0.30	30
P.24	"	17.40	335	10.70	90

OH-PB = Hydroxyl-terminated polybutadiene

TABLE 5

Percentage Changes of Original Mechanical Properties of Polyurethane Elastomers After Ageing

Elastomer No	% change after 28 days in											
	Dry air at 80°C				Water at 80°C				STF at 65°C			
	TS	EB	H	M ₁₀₀	TS	EB	H	M ₁₀₀	TS	EB	H	M ₁₀₀
P.1	+ 50.0	- 82.0	>+ 50.0	-	- 40.0	- 44.0	-	- 51.0	- 50.0	- 68.0	-	-
P.2	- 24.6	- 60.0	+ 20.4	-	- 40.0	- 20.0	+ 16.3	-	Too swollen to test			
P.3	- 10.7	- 33.3	+ 7.0	-	- 18.8	- 11.1	- 2.3	-	- 74.5	- 55.6	- 18.6	-
P.4	- 6.2	- 73.9	+ 53.5	-	- 57.8	- 25.2	- 3.5	-	- 95.9	- 34.8	-	-
P.5	-	-	-	-	- 2.6	- 14.8	- 5.5	- 2.0	- 85.4	- 52.6	- 62.5	- 80.0
P.6	-	-	-	-	0.0	- 2.7	- 5.0	+ 7.5	- 84.8	- 48.3	- 55.4	- 79.3
P.7	-	-	-	-	- 16.3	+ 14.1	- 3.7	+ 8.2	- 82.6	- 50.2	- 35.0	- 55.9
P.8	-	-	-	-	- 38.0	- 18.6	- 5.5	- 1.0	- 87.6	- 58.1	- 31.5	- 66.5
P.9	-	-	-	-	- 47.1	+118.0	- 28.1	- 38.7	- 95.3	- 52.9	- 53.2	-
P.10	-	-	-	-	+ 10.0	- 11.1	+ 4.9	-	- 71.6	- 44.4	- 16.1	-
P.11	-	-	-	-	+ 2.27	- 65.1	0.0	- 9.9	- 72.8	- 58.0	- 25.9	-
P.12	-	-	-	-	- 3.7	- 9.4	- 2.6	-	- 77.7	- 54.3	- 30.7	- 58.2
P.13	-	-	-	-	- 47.1	+118.0	- 28.1	-	- 95.3	- 52.9	- 53.2	-
P.14	-	-	-	-	- 70.0	+120.0	- 45.0	-	- 95.8	- 50.7	- 45.0	-
P.15	-	-	-	-	- 11.8	- 8.8	- 20.7	-	Too swollen to test			
P.16	-	-	-	-	- 5.1	- 2.7	- 7.2	-	- 79.8	- 45.6	- 34.9	- 84.0
P.17	+ 1.5	+ 12.5	-	-	Disintegrated				- 27.3	- 11.3	0.0	+165
P.18	- 77.5	+ 22.2	- 4.5	+100.0	Disintegrated				- 78.8	- 60.0	0.0	-

B

P.17, P.19, P.20, P.23 and P.24 are polyester urethanes

- = not tested or no value recorded

TTS = Tensile strength at break, MN/m²

Extension at break, %

H = Hardness, BS°

M_{100} = Modulus at 100 per cent extension, MN/m^2

APPENDIX B

FORMULATIONS AND
METHODS OF PREPARATION

APPENDIX B

HYDROXYL-TERMINATED POLYBUTADIENE ELASTOMERS P.1 AND P.2

	P.1	P.2
R.45 homopolymer	250 g	-
R.15 homopolymer	-	250 g
TDI 80% 2,4 isomer)	16.25 g	14.75 g
TDI 20% 2,6 isomer)		
**NCO : OH ratio	1.0 : 1.0	1.0 : 1.0

METHOD

To a 500 g one litre three-necked flask equipped with heating mantle stirrer, thermometer and vacuum inlet tube, was added 250 g hydroxyl-terminated polybutadiene polymer. The polymer was degassed at 25°C under 5 mmHg vacuum and stirred continuously for 45 minutes.

TDI was added from a dropping funnel and the mixture stirred a further 15 minutes under vacuum.

**Calculation

$$\text{Wt/TDI per 100 g resin} = \frac{\text{Hydroxyl No Polybutadiene meq/g} \times \text{Eq Wt TDI (NCO/OH ratio)}}{10}$$

$$* 1 \text{ mmHg} = 133.322 \text{ N/m}^2$$

APPENDIX B

TABLE 10

PREPARATION OF PREPOLYMERS P.P.1 - P.P.6 FOR ELASTOMERS P.3 - P.16

	P.P.1	P.P.2	P.P.3	P.P.4	P.P.5	P.P.6
R.45 M homopolymer	-	1000 g	1000 g	-	-	-
R.15 M homopolymer	1000 g	-	-	1000 g	-	-
CS.15 styrene copolymer	-	-	-	-	1000 g	-
CN.15 acrylonitrile copolymer	-	-	-	-	-	1000 g
TDI 80% 2,4 isomer) TDI 20% 2,6 isomer)	305 g	217 g	213 g	310 g	303 g	280 g
Unreacted NCO ₂ content of prepolymer (calculated) %	9.1	6.0	8.25	9.0	9.0	8.7
Unreacted NCO (determined) %	-	-	8.33	-	-	-
General appearance	pale lemon	pale lemon	pale lemon	pale lemon	opaque white	orange
Stability on storage	Cloudy 1 month	Cloudy 1 month	>11month	> 1 month	> 1 month	skinning and thickening 1 month

METHOD

To a two-litre reaction flask, fitted with a detachable four-necked cover, equipped with heating mantle, stirrer, thermometer, and vacuum and nitrogen inlet tubes, was added 1000 g hydroxyl-terminated polybutadiene polymer. The temperature was raised to 110°C over 30 minutes and the resin degassed under 1 mmHg vacuum of 30 minutes. The resin was cooled to 25 - 30°C and TDI was added rapidly (2 to 3 minutes) under nitrogen and stirred continuously for 1 hour. The prepolymers were placed in dried 4 lb Kilner jars flushed with nitrogen and then sealed under nitrogen.

APPENDIX L

CALCULATION

Weight of TDI per 100 g Polybutadiene Resin =

$$\frac{(100)(\text{Equivalent weight of TDI})}{(\text{Equivalent weight Polybutadiene Resin})} \times \frac{100(\text{Equivalent weight NCO})}{100(\text{Equivalent weight NCO})}$$

$$+ \frac{\text{Equivalent weight Polybutadiene}(\% \text{ Free NCO})}{\text{Equivalent weight TDI}(\% \text{ Free NCO})}$$

TABLE 11

Hydroxyl-Terminated Butadiene Polyurethane Elastomers

Elastomer Number	Polymer	Prepolymer Number	Free NCO in Prepolymer	Prepolymer, g	Diol	Diol, g	Diamine	Diamine, g	Mole Ratio NCO : OH or NH	**Carbon Black, g
P.3	R.15m	P.P.1	9.1	250	2-Ethyl hexane -1,3-diol	30.5	-	-	1.3 : 1.0	-
P.4	R.45m	P.P.2	6.0	250	" "	26.1	-	-	1.0 : 1.0	-
(a)P.5	R.45m	P.P.3	8.25	250	" "	32.5	-	-	1.1 : 1.0	-
P.6	R.15m	P.P.4	9.0	250	" "	35.5	-	-	1.1 : 1.0	-
P.7	CS.15	P.P.5	9.0	250	" "	35.5	-	-	1.1 : 1.0	-
P.8	CN.15	P.P.6	8.7	250	" "	34.4	-	-	1.1 : 1.0	-
P.9	R.45m	P.P.3	8.25	250	1,4-Butane diol	20.1	-	-	1.1 : 1.0	-
P.10	R.45m	P.P.3	8.25	250	1,5-Pentane diol	23.2	-	-	1.1 : 1.0	-
P.11	R.45m	P.P.3	8.25	250	1,2-Propene diol	35.5	-	-	1.1 : 1.0	-
P.12	R.45m	P.P.3	8.25	250	2-Ethyl hexane -1,3-diol	35.5	-	-	1.1 : 1.0	-
P.13	CS.15	P.P.5	9.0	250	-	-	Flexsone 4L*	54.3	0.75 : 1.0	-
P.14	CN.15	P.P.6	8.7	250	-	-	" "	52.5	0.75 : 1.0	-
P.15	R.15m	P.P.4	9.0	250	2-Ethyl hexane -1,3-diol	35.5	-	-	1.1 : 1.0	40.0
P.16	CN.15	P.P.6	8.7	250	" "	34.5	-	-	1.1 : 1.0	40.0

Note (a) 0.3 pph dibutyl tin dilaurate catalyst

* N.N'-bis-(1,4-dimethylpentyl)-p-phenylene diamine

P.10	R.45m	P.P.3	8.25	250	1,5-Fantane diol	23.2	-	1.1 : 1.0	-
P.11	R.45m	P.P.3	8.25	250	1,2-Propane diol	35.5	-	1.1 : 1.0	-
P.12	R.45m	P.P.3	8.25	250	2-Ethyl hexane -1,3-diol	35.5	-	1.1 : 1.0	-
P.13	CS.15	P.P.5	9.0	250	-	-	Flexzone 4L*	0.75 : 1.0	-
P.14	CN.15	P.P.6	8.7	250	-	-	"	0.75 : 1.0	-
P.15	R.15m	P.P.4	9.0	250	2-Ethyl hexane -1,3-diol	35.5	-	1.1 : 1.0	40.0
P.16	CN.15	P.P.6	8.7	250	"	34.5	-	1.1 : 1.0	40.0

Note (a) 0.3 pph dibutyl tin dilaurate catalyst

* N,N'-bis-(1,4-dimethylpentyl)-p-phenylene diamine

** Vulcan 3F

Methods of Preparation

P.P.3 - 12

To a 500 ml three-necked reaction flask equipped with heating mantle, stirrer, thermometer dropping funnel and vacuum inlet was added 250 g TDI/polybutadiene prepolymer. This was degassed under moderate vacuum (30 mmHg) for 30 minutes at 65°C. Dibutyl tin dilaurate catalyst was added to P.5 only. The temperature was raised to 75°C and the diol added under vacuum. The mixture was stirred continuously and degassed for 5 minutes under 1 mmHg vacuum.

P.13 - 14

Method as above, except the prepolymer was degassed at 25°C and diamine added under 1 mmHg vacuum.

P.15 - 16

Method as for P.3 - 12, except that 40 g of carbon black was dispersed into 250 g of prepolymer prior to reaction at 65°C.

* Calculation:
$$\frac{\text{Weight of Diol or Diamine}}{100 \text{ g Polybutadiene Prepolymer}} = \frac{(\% \text{ Free NCO in Prepolymer}) (\text{Equivalent weight of Diol or Diamine})}{42(\text{NCO/OH or NH mole ratio})}$$

where Equivalent Weight of Diol or Diamine = $\frac{\text{Molecular weight}}{2}$

B

APPENDIX B

POLYESTER AND POLYETHER URETHANE ELASTOMER P.17 - P.24

The elastomers were prepared by a direct method, except for P.19, P.20 and P.22, which were prepared via a prepolymer method.

The polyesters (molecular weights 1900 - 2100) were prepared in the laboratory to give acid number < 1.0 mg KOH and hydroxyl number 55 - 65 mg KOH/g. The adipic acid was laboratory reagent grade ex-BDH, melting point 152 - 154°C.

All the diols and triols used were laboratory reagent grades and were redistilled under reduced pressure before use.

The butadiene-epichlorhydrin and methyl styrene-epichlorhydrin oligomers were prepared in the laboratory.

The polyethers were obtained from commercial sources.

		<u>Mol Wt</u>	<u>Holes</u>	<u>g</u>
P.17	Polydiethylene adipate	2000	1.0	500.0
	1,2,6-hexane triol	134	0.66	22.0
	TDI	174	2.2	96.0
P.18	*Polypropylene glycol ether	2000	1.0	500.0
	1,2,6-hexane triol	134	0.67	22.5
	TDI	174	2.33	101.25
P.21	**Polytetramethylene glycol ether	1970	1.0	492.0
	1,2,6-hexane triol	134	0.66	22.0
	TDI	174	2.2	96.0
P.23	Polydiethylene adipate	2220	1.0	555.0
	1,2,6-hexane triol	134	0.66	22.0
	TDI	174	2.1	91.5
P.24	Polytetramethylene adipate	2250	1.0	562.0
	1,2,6-hexane triol	134	0.66	22.0
	TDI	174	2.1	91.5
P.22	Polytetramethylene glycol ether (2.8 per cent free NCO)			1000.0
	MCCA			88.0

*Ex-Union Carbide

**Polymeg ex-Quaker Oats Co

	<u>Prepolymer</u>	<u>Mol Wt</u>	<u>Moles</u>	<u>g</u>
P.19, P.20	Polydiethylene adipate	2000	1.0	500
	TDI	174	2.1	91.5

METHOD

To a 1000 ml glass three-necked reactor equipped with mantle, thermometer, stirrer and nitrogen inlet tube was added 91.5 g TDI. The temperature was raised to 80°C and the polyester added over a period of 1 hour. The mixture was stirred under nitrogen for 3 hours at 85°C.

	<u>P.19</u>		<u>P.20</u>	
	<u>Moles</u>	<u>g</u>	<u>Moles</u>	<u>g</u>
Polydiethylene adipate/TDI prepolymer	5	120	2.2	133
Butadiene-epichlorhydrin oligomer	2	16	-	-
Methyl styrene-epichlorhydrin oligomer	-	-	1.0	42

METHOD

In a 250 ml three-necked glass reactor equipped with heating mantle, thermometer, stirrer and vacuum inlet tube was added the prepolymer; this was heated to 85°C with continuous stirring and degassed for 30 minutes under moderate vacuum, 30 mmHg. The chain extender was added and the mixture degassed for 3 minutes under 1 mmHg (P.19 at 85°C and P.20 at 120°C).

S No 137/70/MG